Paramagnetic Intermediates in the Thermal Reactions of Benzo[2,1-*b*;3,4-*b*′]dithiophen-4,5-dione with Some Metal(III) Compounds of the Heavier Group VB Elements

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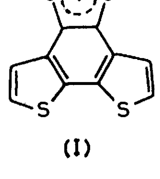
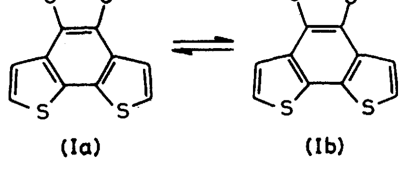
The paramagnetic adducts resulting from the thermal reaction between benzo[2,1-*b*;3,4-*b*′]dithiophen-4,5-dione and some organometallic derivatives of arsenic, antimony, and bismuth have been investigated by e.s.r. spectroscopy. From the e.s.r. data two alternative structural situations can be envisaged for these radicals, which in principle can be depicted either as species containing a four-co-ordinated metal atom (I), or as the average of a rapid equilibrium between two equivalent three-co-ordinate tautomers (Ia and b).

THE reactions of orthoquinones with the halides and organometallic derivatives of the elements of groups IIIB and IVB have been extensively investigated by e.s.r. Leading references to the Russian work in this field are contained in the paper by Prokof'ev and his co-workers on silicon-containing free radicals.[1] Radicals containing phosphorus have been the subject of several communications [2] but the heavier Group VB elements have been less thoroughly studied. An investigation [3] of the reaction of $SbCl_3$ and $SbCl_5$ with some orthoquinones led to e.s.r. signals but these could not be unambiguously assigned. In a recent note [4] we have described radicals formed by the thermal reactions of $SbCl_3$, SbF_3, and $BiPh_3$ with benzo[2,1-*b*;3,4-*b*′]dithiophen-4,5-dione (TQ) and 9,10-phenanthraquinone (PQ). Radicals containing P, As, Sb, and Bi have been obtained by direct reaction of the Group VB elements with orthoquinones.[5] We now report the results of an investigation of the thermal reactions of the compounds $MCl_{3-n}Ph_n$ (M = As, Sb), $AsMe_2Br$, SbF_3, $BiCl_3$, and $BiPh_3$ and a range of heterocyclic compounds containing As^{III} and Sb^{III} with TQ using diglyme, tetraglyme, and molten biphenyl as solvents.

RESULTS

Arsenic and Antimony Derivatives.—As previously reported [4] the reaction of TQ with SbF_3 gives an e.s.r. spectrum which shows hyperfine coupling to a single antimony nucleus (^{121}Sb, ^{123}Sb), two fluorine nuclei, and two protons. We assigned this radical structure (I; M = Sb, $R^1 = R^2$ = F) in which the metal is either four co-ordinated or there is a rapid dynamic equilibrium between the equivalent tautomers (Ia and b).


(I)


(Ia) (Ib)

A related series of radicals are formed from the compounds $MCl_{3-n}Ph_n$ (M = As, Sb). The reactions with MCl_3 and MPh_3 each give a single product, but more complicated behaviour was observed with $MClPh_2$ and MCl_2Ph. The best resolved spectra were obtained for radicals with $R^1 = R^2$ = Cl when, in addition to the metal splittings, couplings to two equivalent chlorine nuclei and two equivalent protons were detected. The spectrum of the radical $[TQAsCl_2]^•$ is shown in Figure 1. The radicals from MPh_3 had larger linewidths and only exhibited resolvable coupling to the metal (^{75}As, ^{121,123}Sb). The reaction with MCl_2Ph gave rise to three overlapping e.s.r. spectra. Two of these were identical with the spectra given by MCl_3 and MPh_3, respectively, and we assign the other signal to the mixed species (R^1 = Ph, R^2 = Cl). This radical was also obtained from $MClPh_2$ along with the MPh_2 adduct. No ^{35}Cl coupling was resolvable in either of the $[TQMClPh]^•$ radicals but a coupling to two equivalent protons was detected for the antimony-containing adduct. The e.s.r. parameters for all these radicals are contained in the Table together with estimates of the spin density in the *s*-orbitals of the metal atoms obtained using the atomic parameters of Morton and Preston.[6] We also include the data for two radicals obtained by heating TQ with $AsMe_2Br$ which we attribute to species with $R^1 = R^2$ = Me and R^1 = Me, R^2 = Br. The assignment has been made by analogy with the AsPhCl adducts.

We have also investigated the thermal reaction of TQ with the heterocyclic compounds (III)—(VI); we assign the radicals produced to the general structure (VII). For example, identical e.s.r. spectra were obtained from (IIIe), (IVa), and (Vc) and we assign them to (VII) with M = Sb and X = Y = O. Similar behaviour was found for the other sets of related heterocycles. No e.s.r. spectra were observed for the phospholes (IIIa and b). The arsoles and stiboles (IIIc—g) each gave weak signals attributable to the MCl_2 adducts in addition to the expected radicals (VII). All these radicals show hyperfine couplings from the metal; the arsenic radicals also show coupling to a pair of equivalent protons similar in magnitude to that found for the MCl_2 adducts. The e.s.r. data are summarised in the Table.

Bismuth Derivatives.—The reactions of TQ with $BiCl_3$ and $BiPh_3$ are less straightforwardly interpreted than those of the arsenic and antimony compounds discussed above. In

E.s.r. parameters for the radicals investigated.

Radical Precursors	Solvent	a_M(200 °C)	$10^3\ \rho_s$	$10^3\ (da_M/dT)$	a (other)
TQ–$AsCl_3$	TG	21.44	4.01	−16.50	1.02 (2 Cl, 2 H)
TQ–$AsCl_3$	BP	21.77	4.16	−19.32	1.03 (2 Cl, 2 H)
TQ–$AsPhCl_2$ TQ–$AsClPh_2$	BP	15.26	2.92	−14.95	No resolved struct.
TQ–$AsPh_3$	BP	19.13	3.66	−18.20	No resolved struct.
TQ–(IIIc)	BP	18.13	3.47	−12.50	0.98 (2 H)
TQ–(IIId)	BP	18.18	3.48	−9.42	0.92 (2 H)
TQ–(VI)	BP	14.66	2.80	−10.10	0.87 (2 H)
TQ–$SbCl_3$	TG	50.36/27.27 [a]	4.02	−21.18	0.96 (2 Cl, 2 H)
TQ–$SbCl_3$	BP	50.39/27.79 [a]	4.02	−16.78	0.96 (2 Cl, 2 H)
TQ–SbF_3	BP	41.41/22.42 [a]	3.31	−17.89	1.09 (2 H, 8.10 (2 F)
TQ–$SbPhCl_2$ TQ–$SbClPh_2$	BP	46.42/25.24 [a]	3.71	−31.57	0.95 (2 H)
TQ–$SbPh_3$	BP	48.18/26.09 [a]	3.85	−25.55	No resolved struct.
TQ–(IIIe)	BP	46.17/25.00 [a]	3.69	−26.84	No resolved struct.
TQ–(IIIf)	BP	44.93/24.33 [a]	3.59	−17.40	No resolved struct.
TQ–(IIIg)	BP	43.39/23.49 [a]	3.47	−19.01	No resolved struct.
TQ–$AsMe_2Br$	BP	19.90 [b]	3.80		No resolved struct.
TQ–$AsMe_2Br$	BP	18.90 [b]	3.61		No resolved struct.
TQ–$BiCl_3$	DG	32.10	1.16	+26.13	No resolved struct.
TQ–$BiCl_3$	TG	32.94	1.19	+19.63	No resolved struct.
TQ–$BiCl_3$	BP	43.92	1.59	−49.10	No resolved struct.
TQ–$BiPh_3$	DG	59.94	2.17	−63.57	No resolved struct.
TQ–$BiPh_3$	TG				
TQ–$BiPh_3$	BP	56.78	2.05	−39.12	No resolved struct.
TQ–$BiPh_3$	BP	50.65	1.83	−31.23	No resolved struct.

DG = Diglyme, TG = tetraglyme, BP = biphenyl.

[a] $^{121}Sb/^{123}Sb$. [b] At 159 °C [coupling constants in G (= 10^4T)].

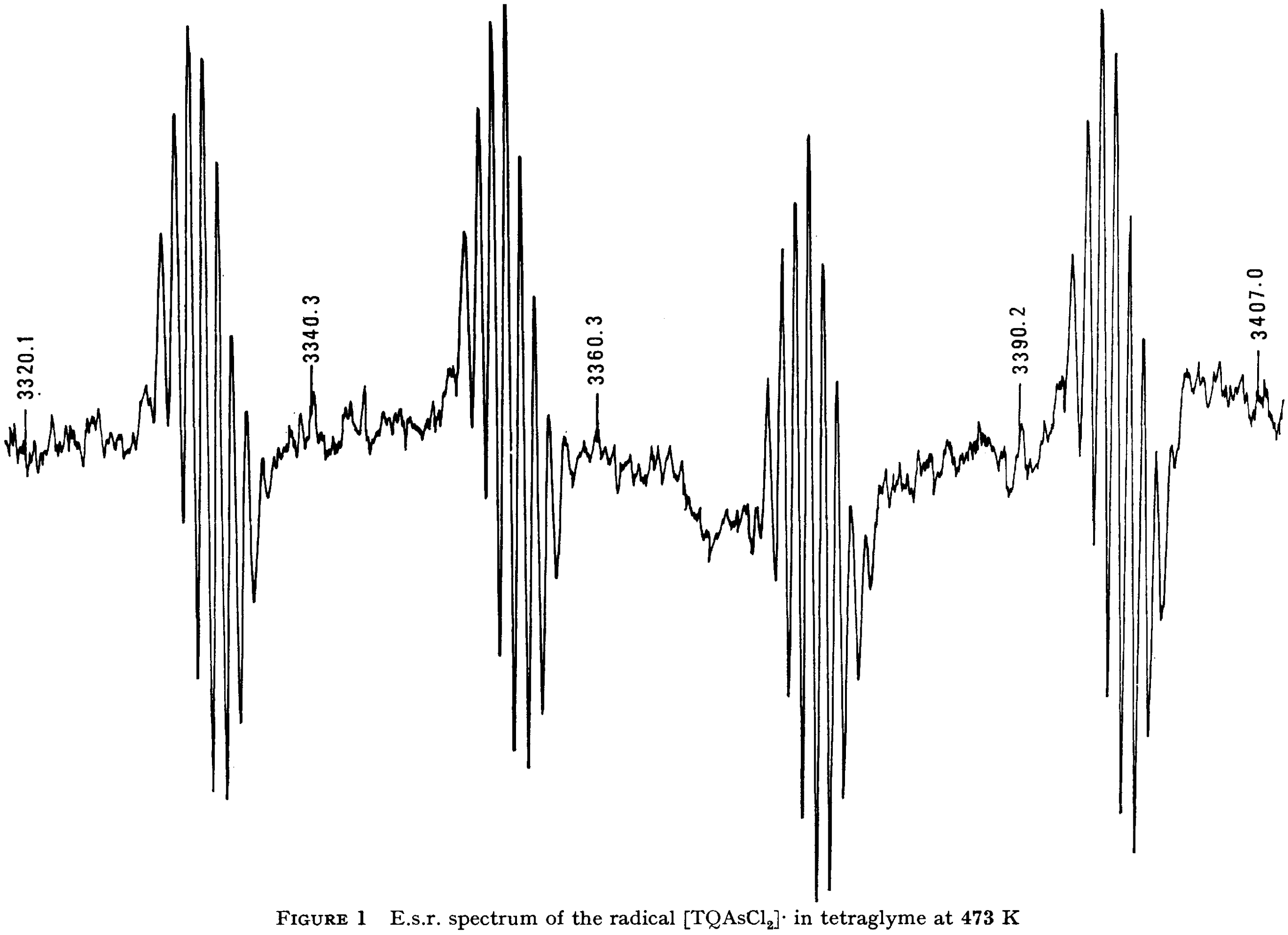
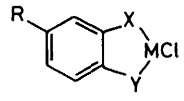
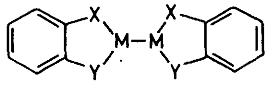


FIGURE 1 E.s.r. spectrum of the radical $[TQAsCl_2]^\cdot$ in tetraglyme at 473 K

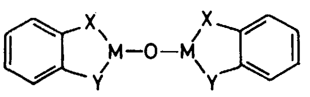
the latter examples no significant variations were found on changing the solvent from diglyme or tetraglyme to molten biphenyl, but this was not the case for $BiCl_3$. In most cases the spectra of the arsenic and antimony radicals exhibited couplings to aromatic ring protons or halogens on the metal but the bismuth spectra had much larger linewidths and only coupling to ^{209}Bi ($I = 9/2$) was resolvable.


(III)

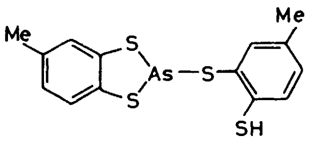
a; X = Y = O, R = H, M = P
b; X = O, Y = S, R = H, M = P
c; X = Y = O, R = H, M = As
d; X = O, Y = S, R = H, M = As
e; X = Y = O, R = H, M = Sb
f; X = O, Y = S, R = H, M = Sb
g; X = Y = S, R = Me, M = Sb

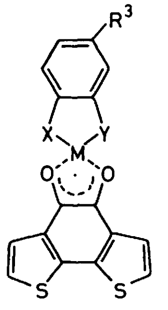

(IV)

a; X = Y = O, M = Sb
b; X = O, Y = S, M = Sb


(V)

a; X = Y = O, M = As
b; X = O, Y = S, M = As
c; X = Y = O, M = Sb
d; X = O, Y = S, M = Sb


(VI)


(VII)

M = As, Sb
X = Y = O, R^3 = H
X = O, Y = S, R^3 = H
X = Y = S, R^3 = Me

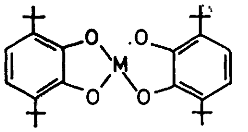
The spectrum obtained from $BiPh_3$ and TQ in diglyme has been reported previously.[4] It shows linewidth variations attributable to quadrupole relaxation of the ^{209}Bi nucleus and only a single species is present. However, in biphenyl at least two, and probably three, bismuth-containing radicals are detectable. The two most abundant species have coupling constants similar to those found for the radical observed in diglyme, but with a different pattern of line-broadening. Whereas in diglyme the outer lines of the spectrum ($m_I = \pm 9/2$) were the sharpest, in biphenyl they were the most broadened.

A similar line-broadening pattern was apparent in the ten-line spectra obtained by heating TQ with $BiCl_3$ in biphenyl or diglyme. However, in the latter case and also in tetraglyme, the ^{209}Bi coupling was smaller and showed a positive temperature dependence; in contrast the metal splittings in all the other species studied exhibited a negative temperature dependence (Table). The two different patterns observed in the linewidths of the bismuth radicals are illustrated in Figure 2.

DISCUSSION

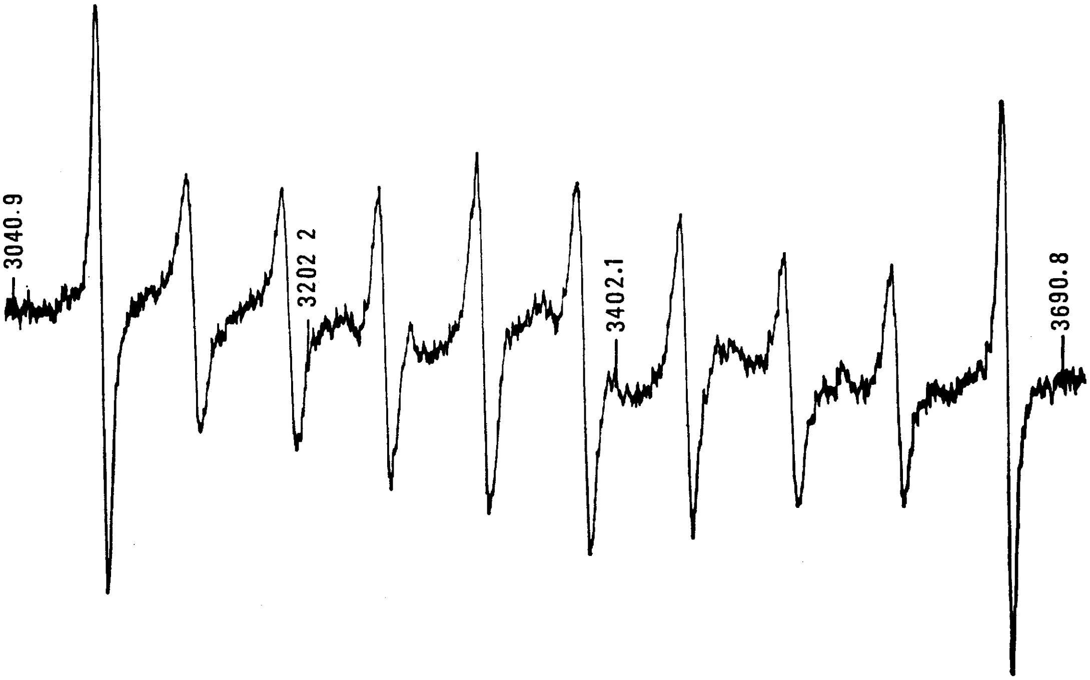
We can be most certain that the assignments we have made above are correct in the case of the radicals derived from $SbCl_3$, SbF_3, and $AsCl_3$. In these species we observe coupling to the halogen nuclei in addition to a splitting from two protons characteristic of the TQ moiety. Similar proton couplings have been observed in adducts of TQ with silicon, germanium, and tin-centred radicals.[7] They are characteristic of a system in which the unpaired electron is largely localised on the ortho-quinone. The assignment of the other radicals we have observed is less conclusive, but the similarity of the metal hyperfine coupling constants indicates that we are dealing with structurally similar species.

Comparable ^{75}As and ^{121,123}Sb splittings have been reported for radicals investigated by Prokof'ev.[5] Much smaller coupling constants are found in derivatives of As^V.


(VIII)

Radical (VIII) with M = As is particularly interesting since it exhibits temperature dependent linewidths in its e.s.r. spectra indicative of a dynamic equilibrium between conformers in which the unpaired electron ' wanders ' between the four oxygen atoms.[8] Unfortunately the thermal methods we have employed to produce our radicals preclude the possibility of obtaining spectra at temperatures much below 100 °C and in no case have we been able to observe any line-broadening characteristic of a dynamic process. We cannot therefore distinguish between structure (I) and a fast exchange between tautomers (Ia and b). However, the substantial coupling constants for ^{19}F and ^{35}Cl observed in the $AsCl_3$, $SbCl_3$, and SbF_3 adducts suggest that these complexes have structure (I) with a four-co-ordinated metal atom. This would be in line with the behaviour found for adducts of the form $[TQSnPh_nCl_{3-n}]^\cdot$ where ^{35}Cl coupling is only resolved when $n = 0$ or 1 and the tin atom is five-co-ordinated.[7] The absence of chlorine coupling in the MPhCl adducts may then be indicative of tautomerism, presumably because in structure (Ia or b) rotation about the O–M bond can lead to averaging of the halogen hyperfine interaction to a value smaller than in (I).

It is interesting to note that in the radicals (VII) the unpaired electron is still localised on the TQ moiety. No



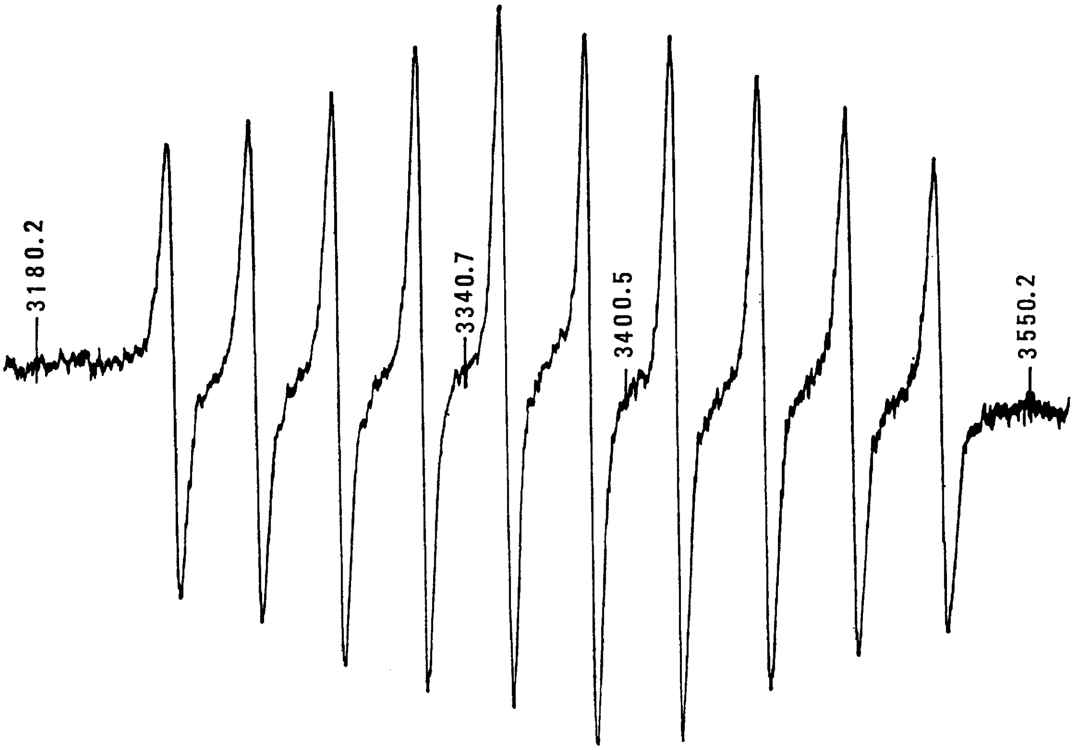
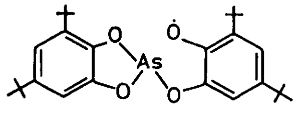


FIGURE 2 (Upper) E.s.r. spectrum of the radical resulting from the reaction between TQ and $BiPh_3$ in diglyme at 393 K. (Lower) E.s.r. spectrum of the radical resulting from the reaction between TQ and $BiCl_3$ in tetraglyme at 413 K

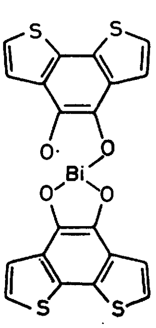
hyperfine coupling was observed for the protons of the other aromatic system. This is consistent with studies of tautomerism in radicals containing phosphorus in which electron exchange was only observed between equivalent ligands.[2] Otherwise the electron remains on the ligand which allows the larger amount of delocalisation.

As we have indicated above the interpretation of our results for bismuth-containing radicals poses more of a problem than the results for arsenic and antimony. The magnitude of the coupling constants indicates comparable spin densities in the metal *s*-orbitals for all three elements and there is little doubt that we are observing species containing Bi^{III}. The reaction with $BiPh_3$ in diglyme procedes smoothly at *ca.* 160 °C and we assign the spectrum to $[TQBiPh_2]^\bullet$. One species observed in molten biphenyl is presumably the same radical but the identity of the second radical is open to speculation. Two spectra with slightly different ^{75}As splittings observed below 60 °C in the reaction of 3,5-di-t-butylorthoquinone with yellow arsenic have been assigned [8] as rotamers of (IX) but it is difficult to envisage a situation in which isomers of $[TQBiPh_2]^\bullet$ could be interconverting slowly on the e.s.r. time scale at 200 °C. Moreover only one radical is observed at lower temperatures in diglyme.



(IX)

The reaction of TQ with $BiCl_3$ in biphenyl gives a radical which could well be $[TQBiCl_2]^\bullet$ but in diglyme or tetraglyme a different species is formed. The main distinguishing feature is the opposite sign found for the temperature dependence of the ^{209}Bi coupling constant. In these solvents we have observed that formation of the radical is preceded by the appearance of a strong e.s.r. signal at *g* 2, similar to that of the TQ radical anion and we suggest that the bismuth-containing species has structure (X) formed by reaction of the semiquinone with $BiCl_3$. A similar radical prepared by reaction of $BiCl_3$ with the potassium semiquinolate of 2,6-di-t-butylorthoquinone (VIII; M = Bi) also exhibits a ^{209}Bi coupling that increases with temperature.



(X)

EXPERIMENTAL

Materials.—Dimethyl(bromo)arsine, trichloroarsine, phenyl(dichloro)arsine, diphenyl(chloro)arsine, triphenylarsine, antimony trichloride, phenyl(dichloro)stibine, diphenyl(chloro)stibine, triphenylstibine, antimony trifluoride, bismuth trichloride, triphenylbismuthine, as well as all the solvents, were commercial products and have been used without further purification.

Benzo[2,1-*b*;3,4-*b'*]dithiophen-4,5-dione (TQ),[9] 2-chloro-1,3,2-benzodioxaphosphole (IIIa),[10] 2-chloro-1,3,2-benzo-oxathiaphosphole (IIIb),[11] 2-chloro-1,3,2-benzodioxa-arsole (IIIc),[12] 2-chloro-1,3,2-benzo-oxathia-arsole (IIId),[12] 2-chloro-1,3,2-benzodioxastibole (IIIe),[13] 2-chloro-1,3,2-benzo-oxathiastibole (IIIf),[13] 2,2'-bi-(1,3,2-benzodioxastibole) (IVa),[13] 2,2'-bi-(1,3,2-benzo-oxathiastibole) (IVb),[13] 2,2'-bi-(1,3,2-benzodioxa-arsole) oxide (Va),[12] 2,2'-bi-(1,3,2-benzo-oxathia-arsole) oxide (Vb),[12] 2,2'-bi-(1,3,2-benzodioxastibole) oxide (Vc),[13] and 2,2'-bi-(1,3,2-benzo-oxathiastibole) oxide (Vd) [13] were prepared according to established procedures. Compounds (IIIg) and (VI) were prepared by the following methods.

2-*Chloro*-5-*methyl*-1,3,2-*benzodithiastibole* (IIIg).—To a stirred solution of 3,4-dimercaptotoluene (50 mmol) in benzene (30 ml) a solution of antimony trichloride (50 mmol) in benzene (20 ml) was added dropwise and the mixture was refluxed until the hydrogen chloride vapours completely disappeared. After cooling, the mixture was poured into diethyl ether and the yellow crystalline precipitate separated by filtration, yield 78%, m.p. 96—98 °C (decomp.), δ ($CDCl_3$) 7.36—6.79 (3 H, m, arom) and 2.28 (3 H, s, CH_3) (Found: C, 27.35; H, 1.8; S, 20.3. Calc. for $C_7H_6ClS_2Sb$: C, 27.0; H, 1.9; S, 20.55%).

2-(2-*Mercapto*-5-*methylphenylthio*)-5-*methyl*-1,3,2-*benzodithia-arsole* (VI).—To a stirred solution of 3,4-dimercaptotoluene (30 mmol) in dry benzene (20 ml) and pyridine (60 mmol), a solution of arsenic trichloride (30 mmol) in dry benzene was added dropwise under an atmosphere of nitrogen. After slowly warming to room temperature, the mixture was filtered and the solvent evaporated *in vacuo*. The residue was purified by column chromatography on silica gel using 3 : 1 diethyl ether–light petroleum as eluant, yield 15%, m.p. 56—58 °C, δ ($CDCl_3$) 7.32—6.77 (6 H, m, arom), 5.24 (1 H, s, SH, D_2O exchanged), and 2.22 (6 H, s, CH_3) (Found: C , 43.4; H, 3.45; S, 33.15. Calc. for $C_{14}H_{13}AsS_4$: C, 43.75; H, 3.4; S, 33.35%).

E.S.R.—The radicals were generated by heating inside the spectrometer cavity sealed Pyrex tubes containing solutions of the reactants (TQ and the appropriate arsenic antimony, or bismuth compound) in diglyme or tetraglyme, or by melting a mixture of the reactants and biphenyl.

The e.s.r. spectra were recorded on Varian E-104 and Bruker ER-200 spectrometers; the magnetic field was calibrated by means of an n.m.r. gaussmeter while the temperature, which was controlled by standard accessories, was measured by means of a copper–constantan thermocouple inserted inside the resonant cavity.

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REFERENCES

[1] A. I. Prokof'ev, T. I. Prokof'eva, I. S. Belostotskaya, N. N. Bubnov, S. P. Solodovnikov, V. V. Ershov, and M. I. Kabachnik, *Tetrahedron*, 1979, **35**, 2471.

[2] A. I. Prokof'ev, T. I. Prokof'eva, I. S. Belostotskaya, N. N. Bubnov, S. P. Solodovnikov, and V. V. Ershov, *Dokl. Akad. Nauk SSSR*, 1979, **246**, 340; S. P. Solodovnikov, N. N. Bubnov, and A. I. Prokof'ev, *Usp. Khim.*, 1980, **49**, 3.

[3] G. A. Abakumov and E. S. Klimov, *Zh. Strukt. Khim.*, 1972, **13**, 922.

[4] A. Alberti and A. Hudson, *J. Organomet. Chem.*, 1979, **182**, C49.

[5] A. I. Prokof'ev, N. A. Malysheva, B. L. Tumanskii, N. N. Bubnov, S. P. Solodovnikov, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1976.

[6] J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577.

[7] A. Alberti, A. Hudson, and G. F. Pedulli, *J. Chem. Soc., Faraday Trans. 2*, 1980, 948.

[8] A. I. Prokof'ev, N. A. Malysheva, N. N. Bubnov, S. P. Solodovnikov, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1969.

[9] G. F. Pedulli, A. Alberti, L. Testaferri, and M. Tiecco, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1701.

[10] P. C. Cofts, J. H. H. Markes, and H. N. Rydon, *J. Am. Chem. Soc.*, 1958, **80**, 4250.

[11] C. Anchisi, L. Corda, A. Maccioni, G. Podda, and M. Secci, *J. Heterocycl. Chem.*, 1979, **16**, 1439.

[12] C. Anchisi, S. Cabiddu, L. Corda, A. Maccioni, and G. Podda, *J. Heterocycl. Chem.*, 1977, **14**, 1331.

[13] C. Anchisi, S. Cabiddu, L. Corda, A. Maccioni, and G. Podda, *J. Heterocycl. Chem.*, 1976, **13**, 1033.